Excitonic Configuration Interaction

Tomislav Piteša, Severin Polonius, Sebastian Mai, Leticia González

Institute of Theoretical Chemistry, University of Vienna, Austria

Nowadays there is a versatile variety of accurate electronic-structure methods for the excited-state calculations, ranging from single-reference (TDDFT, MP/ADC, and EOM-CC etc.) to the multi-reference (CASPT2, MRCI etc.) ones. However, all of these methods scale unfavourably (at least ~N^5) with the system size, and therefore are often not applicable on large molecules, such as e.g. multichromophoric systems. An alternative to the direct treatment of the full system in these cases is to employ an excitonic model. The underlying philosophy of all excitonic models is to obtain the electronic states of individual chromophores (site states), and then construct a set of their antisymmetrized products (excitonic basis). The full-system Hamiltonian is then represented in the excitonic basis and diagonalized. [1] Many of the so-far developed models rely on the famous Frenkel excitonic model, which employs an *ad hoc* parametrization the Hamiltonian in the basis of only local-excitation products – ones having only one site in an excited state. [2]

In this work, we present the Excitonic Configuration Interaction (ECI) method – an excitonic-like approach, which *i*) self-consistently constructs the excitonic basis so that it minimizes the full-system ground-state energy and *ii*) can account for the contributions of both local and non-local excitations to the full-system states. The application of ECI to a strongly-correlated metal complex is presented, as well as the comparison with the raw Frenkel model and with the Frenkel model coupled to the electrostatic-embedding scheme. [3]

[1] F. Segatta; L. Cupellini; M. Garavelli; B. Mennucci; *Chem. Rev.* **119** 9361 (2019)
[2] E. Sangiogo Gil; G. Granucci: M. Persico; *J. Chem. Theory Comput.* **17** 7373 (2021)
[3] M. F. S. J. Menger; F. Plasser, L. González; *J. Chem. Theory Comput.* **14** 6139 (2018)